

PATENT ABSTRACTS OF JAPAN

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(54) NONAQUEOUS BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To restrain the increase of the internal pressure of a battery, keep high airtight over a long period of time and prevent leakage of electrolyte, decrease in the cycle service life and deformation of a vessel by providing a carbon dioxide absorbent composed of a hydroxide oxide and carbonate of a metal of group I and group II in the battery.

SOLUTION: A carbon dioxide absorbent is sealed in a nonaqueous secondary battery. A hydroxide oxide or carbonate of a metal of group I and group II is used as the carbon dioxide absorbent. LiOH , NaOH , KOH , Ca(OH)_2 , Ba(OH)_2 , Li_2O , CaO , Ascarite or the like are given as examples. These compounds absorb carbon dioxide to form carbonates. These compounds are stable solids, easily handled and can be used as a pellet, a small particle or powder. A material using the molecular sieve action, such as synthetic zeolite, activated carbon, molecular sieving carbon or the like can be used as the carbon dioxide absorbent.

CLAIMS

[Claim(s)]

[Claim 1] A nonaqueous cell provided with a carbon dioxide absorber.

[Claim 2] The nonaqueous cell according to claim 1 wherein a carbon dioxide absorber is hydroxide, an oxide and/or carbonate of metal of I and II groups.

[Claim 3] The nonaqueous cell according to claim 1 wherein carbon dioxide adsorption material is carbon dioxide adsorption material using a molecular sieve operation.

[Claim 4] Claims 1 and 2 a nonaqueous cell wherein a nonaqueous cell of three statements uses a solid electrolyte as an electrolyte.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the cell which used the nonaqueous ion conductor.

[0002]

[Description of the Prior Art] When it holds at an elevated temperature by the time of early charge and a charging state in the former for example a lithium cell problemssuch as disclosure of an electrolysis solution modification of a can and a fall of a cycle life arise by the rise of internal pressure. It is possible that the gas which uses the decomposition product of a solvent or an electrolyte as the main ingredients is emitted as this cause by oxidation etc. of the nonaqueous organic solvent by the reaction of lithium etc. and the nonaqueous organic solvent which were intercalated in the lithium metal or carbon of a negative electrode or the positive-electrode-oxidation thing of a charging state. By a cylindrical cell on the other hand JP5-335011A JP6-140012A etc. In the thin cell the method of providing a safety valve as indicated by JP5-13061A and JP7-22705A or the method of controlling generating of carbon dioxide by covering a negative pole material as indicated by JP7-235328A is proposed. The nonwoven fabric sheet which supported activated carbon is provided in the safety valve upper part which exists inside a battery lid at JP7-192775A The method of aiming at reduction of the quantity of the organic solvent spouted at the time of a safe valve action and the method of using hydrogen absorption agentssuch as palladium for JP6-267593A for the purpose of adsorbing the hydrogen to generate are proposed.

[0003] However when the safety valve using elastic bodiesuch as a spring is provided battery structure becomes complicated and also problemssuch as disclosure of the electrolysis solution from a safety valve an airtight fall and a short circuit at the time of a safe valve action arise. When a sealed part with weak intensity is provided and it is made into a safety valve after a safe valve action becomes unusable. In a thin cell modification of the container by an internal pressure rise poses a problem.

[0004]

[Problem(s) to be Solved by the Invention] An object of this invention is to provide the nonaqueous cell which it is possible to hold high airtightness over a long period of time and can prevent disclosure of an electrolysis solution the fall of a cycle life and modification of a container by controlling an internal pressure rise.

[0005]

[Means for Solving the Problem] In order to attain this purpose this invention persons advance examination wholeheartedly find out that the main ingredients of the gas emitted are carbon dioxide and came to complete this invention. That is this invention is 1. A nonaqueous cell provided with a carbon dioxide absorber 2. Nonaqueous cell of the above 1 whose carbon dioxide absorber is hydroxide oxide or carbonate of metal of I fellows and II group and 3. Nonaqueous cell of the above 1 which is the carbon dioxide adsorption material for which carbon dioxide adsorption material used a molecular sieve operation. 4. Provide a nonaqueous cell using a solid electrolyte in the above 1 and 2 or a nonaqueous cell of 3.

[0006] Hereafter this invention is explained in detail. The following are mentioned as a carbon dioxide absorber used in this invention.

1) Hydroxide an oxide or carbonate of metal of I fellows and an II group.

Hydroxide of metal of I fellows and an II group and an oxide absorb carbon dioxide efficiently and also since they are solid they are easy handling. Specifically LiOH , NaOH , KOH , Ca(OH)_2 , Ba(OH)_2 , Li_2O , CaO , Ascarite etc. are raised. These produce carbonate by absorbing with carbon dioxide. Since carbonate of metal of I fellows and an II group reacts to carbon dioxide further and a hydrogencarbonate is produced using as a carbon dioxide absorber is also possible for example CaCO_3 , K_2CO_3 , Na_2CO_3 etc. are mentioned. These are stable and since they are solid they are easy handling. Especially an oxide of hydroxide: Li_2O of LiOH , NaOH , KOH , Ca(OH)_2 and Ba(OH)_2 and CaO is used preferably. Especially in a lithium cell it is preferred to use LiOH and Li_2O .

[0007] These can be used in the state of a pellet, granule, chip or powder. It is made to contain in a film and these can also be used [also using in the state as it is also covering and using with a high resin film of gas permeation nature such as Nafion, cellophane, polyethylene, polypropylene and a polyethylene system stretch film and]. For example in a cell by which consisted of an electrolysis solution and a separator and the exterior was carried out with a metal can, there are a method of coming out as it is without covering or covering a carbon dioxide absorber with a high resin film of gas permeation nature into a portion of a lid, a method of covering with a high resin film of gas permeation nature and putting this absorber into a crevice between a battery element and an outer wall, a method of carrying out the coat of the inside of a can with a film having contained this absorber etc.

[0008] A polyethylene film (BF film trade name) having contained activation calcium carbonate is effective when moisture in a system and capability to absorb carbon dioxide and also to adsorb ethylene also use an electrolysis solution having contained ethylene carbonate from a certain thing. When a solid electrolyte is used since liquid is held at an electrolyte membrane width of selection of a carbon dioxide absorber of a wrap film is wide. When a sheathing material is film state embedding directly on an inside film is also possible. as for Li_2O and LiOH when using for a lithium cell it is possible to also make it for it to be alike and distribute all over a direct electrolysis solution, a solid electrolyte or an electrode active material layer. A method of distributing uniformly as a method of distributing a method of making it locally unevenly distributed and a method of making it exist in layers are mentioned.

[0009] 2) Carbon dioxide adsorption material using a molecular sieve operation. As carbon dioxide adsorption material using a molecular sieve operation carbon system adsorption materials such as 4A type composition zeolites such as the molecular sieve 4A ZEORAMU A-4 and the leakage-at-bulb curite A-430 and activated carbon molecular SHIBINGU carbon is mentioned. Although there are directions for use such as a method of putting into a portion of a lid, a method of putting into a high resin film of gas permeation nature and putting into a crevice and the method of carrying out the coat of the inside of a can with a film having contained an absorber as well as a case of 1) 4A type composition zeolite is inertness electrochemically and since it is also possible to use it into an electrolysis solution, a solid electrolyte or an electrode making it distribute directly its carbon dioxide absorption efficiency is good. 4A type zeolite has high absorbance of carbon dioxide and its adsorption capability of carbon dioxide which is a polar molecule is dramatically high compared with a case where nonpolar molecules such as hydrogen are adsorbed. In order to stick to water etc. it is useful also although

decomposition products other than carbon dioxide and an impurity are adsorbed. Since it acts also as a filler it is useful also although dynamic strength of a solid electrolyte or a separator is maintained.

[0010] When using molecular SHIBINGU carbon the same directions for use as a case of hydroxide of metal of I fellows of 1 and an II group an oxide or carbonate can be considered. Since molecular SHIBINGU carbon is excellent also in adsorption capability of acid etc. it is useful to remove hydrogen fluoride etc. which are produced by electrolytic disassembly.

3) In addition I which has the above and the carbon dioxide absorption power of an iron system other than 1 and 2 such as a deoxidant metal lithium metal calcium and metal magnesium and II group metal are also useful. The same directions for use as a case of hydroxide of metal of I fellows of 1 and an II group an oxide or carbonate are possible for these. It is also possible to fix by making carbon dioxide react to other organic matters chemically. For example beta-aminoethyl alcohol can fix carbon by generating carbonic acid beta-aminoethyl ammonium. In this case it is possible to make to cover and use with a high resin film of gas permeation nature such as

Nafion cellophan polyethylene polypropylene and a polyethylene system stretch film or a nonwoven fabric absorbent to use.

[0011] Nickel and aluminum are used as a positive pole collector and copper is used as a negative pole collector. As an active material used for a positive electrode material alkali metal oxide such as LiCoO_2 Vanadium oxide such as an oxide of other metals such as MnO_2 a multiple oxide with hydroxide and V_2O_5 Transition metal TORIKARUKOGENAITO such as transition metal JIKARUKOGENAITO such as chromium oxidation thing such as Cr_2O_5 TiS_2 MoS_2 and FeS_2 and NbSe_3 a cheveu rel phase $(\text{AxMo}_6\text{Y}_8\text{A}=\text{LiCuY}=\text{SSe})$ etc. are used.

[0012] A conductive polymer etc. which dope a carbon material as an active material used for a negative electrode material which can carry out occlusion of the lithium such as metal lithium a lithium alloy needle coke and graphite and lithium and can be dedoped are used. A carbonate system lithium salt solution a gel system electrolyte and a solid electrolyte can be used as an inter-electrode ion migration medium. As a polymer material of a gel system electrolyte among these a polyvinylidene fluoride system polymer A polyacrylonitrile system polymer etc. are used they are used by ethylene carbonate propylene carbonate gamma-butyrolactone 1,2-dimethoxyethane tetrahydrofuran etc. as an organic solvent and as a solute LiClO_4 LiPF_6 LiBF_4 etc. are used.

[0013] This invention is the cell which equipped an inside of a nonaqueous cell with the aforementioned carbon dioxide absorbent and can constitute a cell from carbon dioxide adsorbent structure corresponding to battery structure to be used. It can use having a carbon dioxide absorber of this invention also as a means to control an internal pressure rise by carbon dioxide generating in a field about electrochemical elements such as not only a nonaqueous cell but a capacitor.

[0014]

[Embodiment of the Invention] Hereafter an example explains this invention still in detail.

[0015]

[Work example 1] The anode and polyvinylidene fluoride (7 cm x 52 cm) (Kynar2850 by Atochem trade name) which consist of 50 cm [6 cm x] LiCoO_2 LiBF_4 / ethylene

carbonate of 1.5M The gel electrolyte swollen with propylene carbonate and 1:1:2 mixed solutions of gamma-butyrolactone and the negative electrode which consists of carbon (6 cm x 50 cm) were laminated the terminal was taken with the film made from SUS from an anode and each negative electrode and it was considered as 5 chip boxes. The layered product used as this 5 chip box is put into the bag which consists of a laminated film of 7cmx13cmx0.5cm polyethylene terephthalate / aluminum / polyethylene (PET/aluminum/PE) (product made from Asahi Chemical Poly Flex time) Furthermore the polyethylene system stretch film (SANTEKKUSUS by Asahi Chemical Industry Co.Ltd. trade name) was used inside this bag and after putting in the bag which enclosed 0.1g of CaO(s) (made by Wako Pure Chem) thermal melting arrival of the mouth of the bag which consists of a PET/aluminum/PE laminated film was carried out. The capacity of the obtained cell was 900mAh. After charging thoroughly when it held at 80 ** for 6 hours the bag which consists of a PET/aluminum/PE laminated film did not swell at all.

[0016]

[Work example 2] Instead of the gel system electrolyte which consists of polyvinylidene fluoride used in Example 1 The layered product used as 5 chip boxes like Example 1 was obtained using LiBF₄ / ethylene carbonate of 1.5M propylene carbonate and the gel electrolyte that swelled 1:1:2 mixed solutions of gamma-butyrolactone to the polyacrylonitrile which constructed the bridge. This was put into the bag of a PET/aluminum/PE laminated film the polyethylene system stretch film was further used inside this bag and after putting in the bag which enclosed 0.6g of ZEORAMU A-4 (TOSOH Make) thermal melting arrival of the mouth of the bag of a PET/aluminum/PE laminated film was carried out. After charging thoroughly when it held at 80 ** for 6 hours the bag did not swell at all.

[0017]

[Work example 3] Instead of the gel system electrolyte which consists of polyvinylidene fluoride used in Example 1 The layered product used as 5 chip boxes like Example 1 was obtained using LiBF₄ / ethylene carbonate of 1.5M propylene carbonate and the gel electrolyte that swelled 1:1:2 mixed solutions of gamma-butyrolactone to the polyacrylonitrile which constructed the bridge. This was put into the bag of a PET/aluminum/PE laminated film the polyethylene system stretch film was further used inside this bag and after putting in the bag which enclosed 0.6g of molecular SHIBINGU carbon (made by Takeda Chemical Industries Ltd.) thermal melting arrival of the mouth of the bag of a PET/aluminum/PE laminated film was carried out. After charging thoroughly when it held at 80 ** for 6 hours the bag did not swell at all.

[0018]

[Comparative example 1] The cell was created like Example 1 except not enclosing a carbon dioxide absorber. After charging thoroughly when it held at 80 ** for 6 hours the bag swelled greatly.

[0019]

[Effect of the Invention] The cell of this invention is excellent in a cycle characteristic and a high temperature conservation characteristic and dramatically useful industrially.